# Effects of Crystal Structure on the Electrochemical Behavior of Boron-doped HTHP Diamond Electrodes

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## INTRODUCTION

Comparative studies of chemical-vapor-deposited single-crystal and polycrystalline diamond thin-film electrodes, grown by the hot-filament techniques, as well as amorphous diamond-like carbon electrodes, revealed some aspects of the role of crystal structure in the electrochemical behavior of diamond [1]. In particular, the electrode behavior of polycrystalline diamond films is mainly determined by the diamond crystallites, rather than is contributed to by the intercrystallite boundaries [2]. The high-temperature-high-pressure single crystals well resemble the CVD thin films in their electrochemical properties [3].

In this work electrochemical properties of individual crystal faces of the HTHP diamond single crystals were studied. The acceptor concentration was determined by differential capacitance measurements; the electrochemical activity of the faces, by taking cyclic voltammograms in the $Fe(CN)_6^{3-/4-}$ system.

## EXPERIMENTAL

The boron-doped diamond single crystals were grown from a boron-containing Ni—Fe—C melt. The growth was performed, using a seed, by the temperature gradient techniques (see [4, 5] for details). The batch contained 0.01 or 0.1 wt. % of boron, which resulted in fabricating moderately or heavily doped crystals.

The crystals are cubo-octahedrons whose basal plane is a (111) growth face. The opposite face was ground and polished. The samples' lateral faces make a combination of cube (100) and octahedron (111) facets of lesser size, as well as the rhombododecahedron (110) and tetragontrioctahedron (211) faces. Ohmic contacts to the rear side of the crystals were made using silver epoxy. The octahedron, cube, and tetragontrioctahedron faces were consecutively exposed to the electrolyte, the rest of the crystals' surface being insulated by high-purity paraffin.

The potentiodynamic curves for 0.01 M $Fe(CN)_6^{3-}$ reduction or $Fe(CN)_6^{4-}$ oxidation were taken, with a linear potential scanning, using a PI-50-1 potentiostat. The differential capacitance was measured over the 20 Hz to 200 kHz frequency range using a Solartron spectra analyzer (model 1250) or an R-5021 ac bridge.

## RESULTS AND DISCUSSION

The impedance spectra showed a specific type of frequency dependence of the differential capacitance, represented by a constant-phase element (CPE) in the electrodes' equivalent circuit. Typical Mott—Schottky plots (that is, the reciprocal of capacitance C squared vs. potential E dependences) are shown in Figure for two principal faces of a heavily doped crystal. From the slope of the lines, the uncompensated acceptor concentrations in the growth sectors associated with the crystal faces were calculated. For the sample under discussion, they are 5 $10^{19}$ and 1.2 $10^{19}$ cm$^{-3}$ for the (100) and (111) faces, respectively.
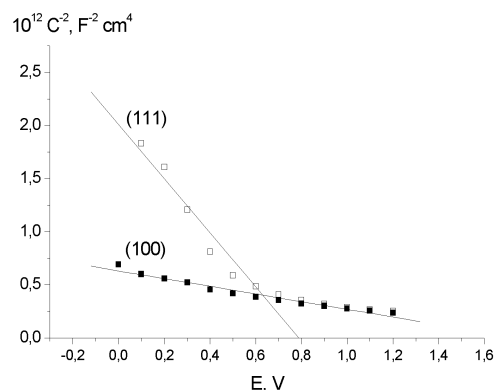


Mott—Schottky plots for the (100) and (111) crystal faces

We see that the (100) face turned to be more heavily doped than the (111) face; this is true for both heavily doped and moderately doped crystals. Surface polishing did not affect significantly the measured capacitance: no difference was found between the basal (growth) and the rear (polished) (111) faces. The (211) face appeared to be rather lightly doped, so we failed in measuring its impedance characteristics. For any face, the acceptor concentration grows with increasing boron concentration in the source melt.

The degree of reversibility of the electrochemical reaction was qualitatively judged by the potential difference for the anodic and cathodic current peaks $\Delta E_p$ on cyclic voltammograms in the $Fe(CN)_6^{3-/4-}$ system.. Kinetic characteristics (transfer coefficients and rate constants) were determined for the individual crystal faces from the dependence of current peak potentials on the potential-scan rate. The (111) face appeared to be most "electrochemically active"; on the (211) face, the reaction was blocked.

## ACKNOWLEDGMENT

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